

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B65D 25/34, B28B 19/00 B05D 1/36	A1	(11) International Publication Number: WO 92/19505 (43) International Publication Date: 12 November 1992 (12.11.92)
(21) International Application Number: PCT/US92/01371 (22) International Filing Date: 24 February 1992 (24.02.92) (30) Priority data: 691,660 26 April 1991 (26.04.91) US (71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US). (72) Inventors: NIEDERST, Ken, W. ; 4735 Lucy Drive, Allison Park, PA 15101 (US). ZERN, John, R. ; 39 Magill Drive, R.D. 2, Cheswick, PA 15024 (US). SEINER, Jerome, A. ; 5415 Plainfield Street, Pittsburgh, PA 15217 (US).	(74) Agents: UHL, William, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al. (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>	
(54) Title: PRESSURIZABLE THERMOPLASTIC CONTAINER HAVING AN EXTERIOR POLYURETHANE LAYER AND ITS METHOD OF MAKING		
(57) Abstract <p>Pressurizable thermoplastic containers, such as those made from polyethylene terephthalate containing a polyurethane layer on the exterior surface thereof are disclosed. The polyurethane layer which is typically applied by a coating process provides the bottle with resistance to stress cracking. The containers are useful as refillable bottles for carbonated beverages which have a tendency to stress crack.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MI	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NI	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

WO 92/19505

PCT/US92/01371

- 1 -

5

PRESSURIZABLE THERMOPLASTIC CONTAINER
HAVING AN EXTERIOR POLYURETHANE LAYER
AND ITS METHOD OF MAKING

10

Background of the Invention

Field of the Invention: The invention relates to
15 thermoplastic containers such as bottles, and more particularly, to
such containers with outer layers of a dissimilar material so as to
provide improved properties to such container. The invention also
relates to a process for preparing such containers.

Brief Description of the Prior Art: Blow molded, plastic
20 bottles such as those made from polyethylene terephthalate have
largely replaced heavier glass bottles previously used for carbonated
beverages and the like. One disadvantage associated with plastic
bottles is the extremely thin wall construction of the body of the
bottle. The bottles are inherently weak which prevents them from
25 being returned to the bottler and refilled.

In an attempt to overcome the above-mentioned disadvantages,
the plastic bottle industry has been manufacturing plastic bottles of
a one-piece construction with thicker body walls. This makes the
bottles stronger enabling them to be returned to the bottler for
30 refilling.

However, in manufacturing bottles of a one-piece
construction with thicker walls, it has been found that such bottles
have a serious stress cracking problem associated with them. Stress
cracking is the development of fine cracks which are the result of
35 the release of stresses introduced into the bottle during the molding
process. Such bottles are manufactured by the blow molding process
which stresses the more rigid side walls of the bottles. The stress
is particularly in the base area of the bottles which is complexly

WO 92/19505

PCT/US92/01371

- 2 -

configured so as to make the bottle free standing. The complex shapes are difficult to mold without stress. In addition, it has been found that stress introduced into the bottles in the blow molding process is accentuated when the bottles are returned to the bottler for reuse. Before refilling the returned bottles, the bottles are given a hot caustic wash and after a number of washes and refillings involving pressurizing the bottles and abrading the base area of the bottle on a conveyor, hazing or stress cracking develops almost exclusively on the exterior surfaces of the bottle. If severe enough, the stress cracking can result in loss of pressure and premature rupturing of the bottles.

It has been found that this stress cracking can be significantly minimized by applying to the exterior surface of the thermoplastic bottles a protective layer of a polyurethane.

15

Summary of the Invention

In accordance with the invention, a pressurizable thermoplastic container with a polyurethane layer on its exterior surface is provided. The container can be subjected to multiple hot caustic washings and refillings with carbonated beverages with minimal, if any, stress cracking. Such containers can be prepared by applying, typically by a coating process, a continuous film of a polyurethane over the exterior surface of the thermoplastic container.

25

Prior Art

U.S. 2,830,721; 2,836,318 and 2,836,319 disclose plastic containers such as polyethylene with an internal and/or an exterior coating of a cured epoxy resin to prevent permeation of the polyethylene by organic liquids.

30

U.S. 2,860,801 and 2,985,542 disclose containers such as polyethylene plastic containers containing a coating based on a vinyl chloride-vinyl acetate-vinyl alcohol terpolymer and an alcoholic-type urea-formaldehyde resin to prevent permeation of the polyethylene by organic liquids.

35

U.S. 3,279,940 discloses polyethylene and polypropylene containers coated with a polyester resin to improve appearance,

WO 92/19505

PCT/US92/01371

- 3 -

abrasion resistance, barrier properties, printability and other characteristics.

U.S. 3,823,032; 4,093,759 and 4,409,266 disclose glass bottles coated with an outer polyurethane layer to prevent scattering
5 of broken glass.

U.S. 4,069,933 discloses a polyethylene terephthalate bottle for carbonated beverages having an interior liquid contacting surface having an effective wetting amount of oleic acid to cover microflaws to reduce nucleation and carbonation loss.

10 U.S. 4,569,869 discloses a polyethylene terephthalate bottle having a UV-cured methyl methacrylate resin outer coating for better wear resistance and smoothness.

U.S. 4,496,517 discloses a process for preparing a polyethylene terephthalate bottle whereby the residual strain of the
15 bottle is reduced by controlling the temperature in the blow molding process.

Detailed Description

The pressurizable thermoplastic materials used in the
20 container construction of the present invention are those which are capable of being blow molded to a rigid structure such that they can withstand being pressurized, typically by containing carbonated beverages. The pressurizable thermoplastic material should be able to withstand up to 100 psi (gauge) pressure. Such materials include
25 crystalline polyolefins such as high density polyethylene and polypropylene and preferably orientable thermoplastic materials, that is, a plastic material which when oriented such as by blow molding increases in strength. Examples of saturated polyesters would be polyethylene terephthalate and other thermoplastic materials of the
30 polyester or polyamide type such as polyhexamethylene adipamide, polycaprolactam, polyhexamethylene sebacamide, poly(ethylene)-2,6- and 1,5-naphthalate and poly(tetramethylene)-1,2-dioxybenzoate. The preferred thermoplastic is polyethylene terephthalate.

The containers of the present invention are manufactured by
35 the blow molding process in which a thermoplastic intermediate article is formed by injection molding. The intermediate article is

WO 92/19505

PCT/US92/01371

- 4 -

of a tubular shape having an opening at its top. A neck portion at the top is shaped preferably in the same shape as that of the final product. A lower part intermediate is closed to form a bottom. After injection molding, the intermediate article is cooled and
5 inserted into a blow mold and a perforated rod connected to a compressed air source inserted downwardly into the intermediate article through its neck portion. The assembly is sealed, the intermediate article heated while blowing air through the perforated rod to expand the intermediate article to the final shape of the
10 container. After expansion of the intermediate article to the shape of the mold, the mold is then cooled and the bottle discharged.

The blow molding process is conducted such that the resultant blow molded container has a relatively thick wall construction, typically on the order of 22 to 26 mils for returnable
15 bottles or a relatively thin wall construction, typically on the order of 12 to 15 mils for non-returnable bottles. For returnable bottles, the amount of plastic contained in the containers of the present invention is approximately twice as much as that which is used with non-returnable thermoplastic containers, typically for a
20 polyethylene terephthalate bottle from 55 to 60 grams per 2-liter bottle as opposed to about 110-115 grams per 2-liter bottle in a returnable polyethylene terephthalate bottle. In addition, the base portion of the bottle contains a base enabling the bottle to be self-standing. Typically, the base can be in the so-called champagne
25 base variety having a rim portion surrounding an inwardly sloping base portion such as are described in U.S. Patent 4,780,257. Alternately, the bottle can be blow molded in a way such that it has a number of protruding feet molded into the base area. Such bottles are well known in the art and are manufactured by Johnson Controls
30 Inc. as BIG FOOT bottles.

The polyurethanes which are useful in the practice of the invention are preferably thermosetting polyurethanes such as those based on a polymeric polyol and an organic polyisocyanate including blocked polyisocyanates. Moisture-curable polyurethanes can also be
35 used. Examples of polymeric polyols are polyether polyols, polyester polyols, acrylic polyols and mixtures thereof. The preferred polyols

WO 92/19505

PCT/US92/01371

- 5 -

are polyester polyols and acrylic polyols because they provide the best balance of properties to the molded bottles such as hardness, scratch resistance, durability, adhesion, flexibility and alkali resistance. Examples of organic polyisocyanates are monomeric
5 polyisocyanates and polymeric isocyanates, with polymeric polyisocyanates being preferred because they are less likely to leave extractable low molecular weight materials.

Examples of polyester polyols are those prepared by the polyesterification of an organic polycarboxylic acid or anhydride
10 thereof with organic polyols and/or an epoxide. Usually, the polycarboxylic acids and polyols are aliphatic or aromatic dibasic acids and diols.

The diols which are usually employed in making the polyester include acyclic alkylene glycols, such as ethylene glycol, neopentyl
15 glycol and cyclic glycols such as hydrogenated bisphenol A, cyclohexanediol and cyclohexanedimethanol. Polyols of higher functionality can also be used. Examples include trimethylolpropane and pentaerythritol, as well as higher molecular weight polyols such as those produced by oxyalkylating low molecular weight polyols.

20 The acid component of the polyester consists primarily of monomeric carboxylic acids or anhydrides having 2 to 18 carbon atoms per molecule. Among the acids which are useful are phthalic acid, terephthalic acid, hexahydrophthalic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, chlorendic acid, decanoic
25 acid and dodecanoic acid. There may be employed higher polycarboxylic acids such as trimellitic acid and tricarballic acid. Where acids are referred to above, it is understood that anhydrides of those acids which form anhydrides can be used in place of the acid. Also, lower alkyl esters of the acids such as dimethyl
30 glutarate and dimethyl terephthalate can be used.

Besides polyester polyols formed from polybasic acids and polyols, polylactone-type polyesters can also be employed. These products are formed from the reaction of a lactone such as epsilon-caprolactone and an active hydrogen-containing compound such
35 as a polyol. Such products are described in U.S. Patent No. 3,169,945 to Hostettler.

WO 92/19505

PCT/US92/01371

- 6 -

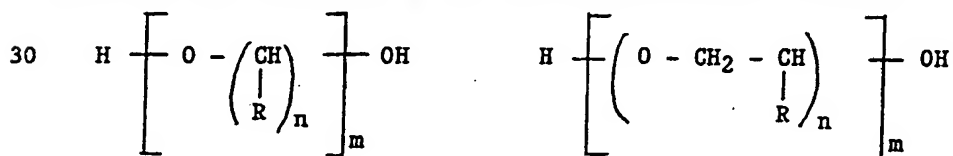
In addition to the polyester polyols, hydroxy-containing acrylic polymers or acrylic polyols can be used as the polyol component.

Among the acrylic polymers are interpolymers of about 2 to 5 30 percent by weight hydroxy-containing vinyl monomers such as hydroxyalkyl acrylate and methacrylate having 2 to 6 carbon atoms in the alkyl group and 90 to 99.8 percent by weight of other ethylenically unsaturated copolymerizable materials such as alkyl acrylates and methacrylates; the percentages by weight being based on 10 the total weight of the monomeric charge.

Examples of suitable alkyl acrylates and methacrylates are methyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate and n-butyl acrylate.

Besides the acrylates and methacrylates, other 15 copolymerizable monomers which can be copolymerized with the hydroxyalkyl acrylates and methacrylates are ethylenically unsaturated materials such as monoolefinic and diolefinic hydrocarbons, halogenated monoolefinic and diolefinic hydrocarbons, unsaturated esters of organic and inorganic acids, amides and esters 20 of unsaturated acids, nitriles and unsaturated acids and the like. Examples of such monomers include styrene, 1,3-butadiene, acrylamide, acrylonitrile, alpha-methyl styrene, alpha-methyl chlorostyrene, vinyl butyrate, vinyl acetate, allyl chloride, divinyl benzene, diallyl itaconate, triallyl cyanurate and mixtures thereof. Usually 25 these other ethylenically unsaturated materials are used in admixture with the above-mentioned acrylates and methacrylates.

Examples of polyether polyols are polyalkylene ether polyols which include those having the following structural formula:



35 where the substituent R is hydrogen or lower alkyl containing from 1 to 5 carbon atoms including mixed substituents, and n is typically from 2 to 6 and m is from 10 to 100 or even higher. Included are poly(oxytetramethylene) glycols, poly(oxyethylene) glycols,

WO 92/19505

PCT/US92/01371

- 7 -

poly(oxy-1,2-propylene) glycols and the reaction products of ethylene glycol with a mixture of 1,2-propylene oxide and ethylene oxide.

The polyisocyanates which may be used in the practice of the invention include aromatic and aliphatic polyisocyanates with 5 aliphatic polyisocyanates being preferred because of their superior ultraviolet light stability and non-yellowing tendencies. Examples of suitable polyisocyanates include monomeric polyisocyanates such as toluene diisocyanate and 4,4'-methylene-bis-(cyclohexyl isocyanate), isophorone diisocyanate and NCO-prepolymers such as the reaction 10 products of monomeric polyisocyanates such as those mentioned above with polyester or polyether polyols. Particularly useful isocyanates are the isocyanurate from isophorone isocyanate commercially available from Chemische Werke Huls AG as Tl890 and the isocyanurate from 1,6-hexamethylene diisocyanate commercially available from Bayer 15 as DESMODUR N.

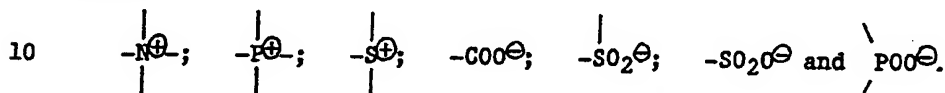
Polyfunctional isocyanates with free isocyanate groups can be used to form two-package room temperature curable systems. In these systems, the polyester and isocyanate curing agents are mixed just prior to their application. Two-package systems are preferred 20 because of their reactivity at low temperature and the fact that they will be applied to temperature-sensitive plastic substrates. The polyurethane layer can be applied to the exterior surface of the thermoplastic substrate as a continuous film by a coating process. For coating applications, a liquid diluent is usually present with 25 the polyurethane to form a coating composition. By liquid diluent is meant a solvent or non-solvent which is volatile and is removed after the coating is applied and is needed to reduce viscosity sufficiently to enable forces available in simple coating techniques, that is, brushing and spraying, to spread the coating to controllable, desired 30 and uniform thicknesses. Generally, a diluent is present in the composition in amounts of about 20 to 90, preferably 50 to 80 percent by weight based on total weight of diluent and polyurethane. Examples of suitable liquid diluents are those which will not attack the thermoplastic bottle and include aromatic hydrocarbons such as 35 toluene and xylene, ketones such as methyl amyl ketone and methyl isobutyl ketone.

WO 92/19505

PCT/US92/01371

- 8 -

When water is employed as a diluent either alone or in admixture with water-miscible solvents, the compositions of the invention should be modified so that they are dispersible in the aqueous diluent. This can be accomplished by the use of externally added emulsifier incorporating water-solubilizing groups such as ethylene oxide moieties or ionic salt groups into one or more of the components of the present invention. Examples of suitable ionic salt groups are:



The ionic salt groups can be incorporated into the components of the coating compositions by techniques well known in the art such as described in U.S. Patent No. 4,147,679 to Scriven et al and in U.S. Patent No. 3,479,310 to Dieterich et al. Waterborne polyurethanes should be well crosslinked. Cationic polyurethanes are preferred because of their resistance to caustic.

For low temperature curing a catalyst such as a tin compound, for example, dibutyltin dilaurate, is usually present in the coating compositions. The catalyst is typically used in amounts of 0.25 to 0.30 percent by weight based on weight of resin solids.

In addition to a diluent, the coating composition will usually contain ingredients such as anti-oxidants, ultraviolet light absorbers, flow control agents, slip agents and anti-mar agents. These materials will typically constitute about 2-10 percent by weight of the coating composition based on weight of resin solids. The anti-oxidant and ultraviolet light absorber protect the bottle from the effects of exterior weathering which causes yellowing of the bottle and poor caustic resistance. The slip agents and anti-mar agents provide abrasion and scratch resistance to the bottle and any printed labels on the bottle.

The coating compositions can be applied by conventional methods including brushing, dipping, flow coating, etc., but preferably are applied by spraying. Usual spray techniques and equipment are used.

WO 92/19505

PCT/US92/01371

- 9 -

The coating operation may be conducted either in a single stage or by a multiple stage coating procedure as is well known in the art. Satisfactory results can be obtained with coatings having a dry film thickness of from about 0.2 to 1.5 mils, preferably from about 0.5 to 0.8 mils. Coating thicknesses less than 0.2 mils are not desired because they provide insufficient resistance to stress cracking and to abrasion. Coating thicknesses greater than 1.5 mils are not desired because of difficulty in curing such coatings in short periods of time. The coating can be applied to the entire exterior surface of the bottle or to portions of the bottle. For example, with non-returnable polyethylene terephthalate bottles with the protruding feet molded into the base area, stress cracking is a particular problem in the areas between the feet. Application of the polyurethane coating in the base area only dramatically increases the resistance to stress cracking. Since the bottle is non-returnable and will not be subjected to repeated caustic washing and pressurized refilling, coating the remaining portions of the bottle is not necessary.

The conditions adopted for curing the thermosetting polyurethane vary somewhat according to the thickness of the coating, the composition of the polyurethane including the presence or absence of catalyst and the sensitivity of the thermoplastic to temperature. Typically, the coating is cured at a temperature of from about 20° to 60°C. for about 30 seconds to 4 hours. Generally, lower temperatures require longer cure times. For example, room temperature compositions (20-25°C.) usually require a 20 minute to 4 hour time period to develop sufficient cure. Infrared heating can be used to shorten the time to handleability.

The following Examples and Comparative Example illustrate the present invention in greater detail but it should not be taken as limiting the invention to their specific details. All parts and percentages are by weight unless otherwise indicated.

In Examples 1-5, various polyurethane coating compositions were prepared and applied to returnable polyethylene terephthalate bottles which were prepared by the blow molding technique.

Comparative Example 6 shows the preparation of a thermosetting

WO 92/19505

PCT/US92/01371

- 10 -

epoxy-amine coating composition which was also applied to a polyethylene terephthalate bottle. The coatings were cured and the coated bottles evaluated for stress cracking by subjecting them to multiple cycles of hot caustic washing, pressurizing and conveyor abrasion. The results are reported in the Table following the Examples.

Example 1

A two-package polyurethane coating composition based on an acrylic polyol and an aliphatic polyisocyanate was prepared from the following ingredients:

Acrylic Polyol Package

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
	Acrylic polyol ¹	4807.87
15	TINUVIN 328 ²	70.27
	TINUVIN 292 ³	70.27
	Wax ⁴	23.4
	Dibutyltin dilaurate	7.06
	Methyl amyl ketone	600.43
20	Silicone ⁵	9.37
	Methyl isobutyl ketone	4202.85

¹ Acrylic polyol available from Henkel Corporation under the trademark G-CURE.

² TINUVIN 328 is a substituted benzotriazole anti-oxidant available from Ciba-Geigy Corporation.

³ TINUVIN 292 is a hindered amine ultraviolet light stabilizer available from Ciba-Geigy Corporation.

⁴ Wax available from Diamond Shamrock Company as S-379N3.

⁵ Silicone available from General Electric Corp. as SF-1023.

30

Polyisocyanate Package

<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
DESMODUR N-3300 ¹	1317.87

¹ Isocyanurate from 1,6-hexamethylene diisocyanate available from Mobay Chemical Company.

WO 92/19505

PCT/US92/01371

- 11 -

The two packages were stirred together to form a coating composition which was spray applied to a 1.5 liter polyethylene terephthalate refillable carbonated beverage bottle. The coating was cured in an electric fired oven at 60°C. for 10 minutes. The bottles were evaluated for stress cracking by subjecting them to cyclic testing consisting of hot caustic washing, pressurizing and conveyor abrasion. The results of the testing are reported in the Table below.

Example 2

10 A two-package polyurethane coating composition based on the polyester polyol and an aliphatic polyisocyanate was prepared from the following ingredients:

Polyester Polyol Package

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
15	Polyester polyol ¹	2639.17
	TINUVIN 328	77.78
	TINUVIN 292	77.78
	S-379N3 wax	25.89
	Dibutyltin dilaurate	1.27
20	Methyl amyl ketone	819.20
	Methyl isobutyl ketone	4800.34
	SF-1023	10.40

¹ Polyester polyol obtained from condensing a polycaprolactone triol (PCP-0301 from Union Carbide Corporation) and 25 azelaic acid in a 2:1 molar ratio.

Polyisocyanate Package

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
	DESMODUR N 3300	2658.58
30	The two packages were stirred together to form a coating composition which was spray applied to a 1.5 liter polyethylene terephthalate refillable carbonated beverage bottle. The coating was cured in an electric fired oven at 60°C. for 15 minutes. The coated bottles were evaluated for stress cracking as described in Example	
35	1. The results are reported in the Table below.	

PCT/US92/01371

- 12 -

A two-package polyurethane coating composition based on a mixture of polyester polyols and aliphatic polyisocyanates was prepared from the following ingredients:

Ingredients

Polyester polyol of Example 2	158.90
Polycaprolactone polyol ¹	59.50
TINUVIN 328	6.45
TINUVIN 292	6.45
SLIP-AYD SL18 ²	10.75
Dow Corning Additive 11 ³	0.43
Methyl amyl ketone	119.29
Methyl isobutyl ketone	286.31

15 1 The polycaprolactone polyol was obtained from ring opening
epsilon-caprolactone with dimethylhydantoin (DANTOCOL DHE) in about a
1 to 1 weight ratio, number average molecular weight 400-500.

2 SLIP-AYD SL18 is a polyethylene dispersion in 2-butoxyethanol from Daniels Products.

20 ³ Dow Corning Additive 11 is a silicone glycol (10% by weight in toluene).

Ingredients

25	DESMODUR N 3300	210.0
	CORONATE 2094 ¹	25.40
	Dibutyltin dilaurate	1.07

¹ CORONATE 2094 is a difunctional prepolymer of 1,6-hexamethylene diisocyanate available from Tosoh USA Inc. through Nippon Polyurethane Industry Co., Ltd.

The two packages were stirred together to form a coating composition which was spray applied to a 1.5 liter polyethylene terephthalate refillable carbonated beverage bottle. The coating was cured in an electric oven at 60°C. for 15 minutes. The coated 35 bottles were evaluated for stress cracking as described in Example

1. The results are reported in the Table below.

WO 92/19505

PCT/US92/01371

- 13 -

Example 4

A two-package polyurethane coating composition based on a mixture of a polycarbonate polyol and a polyisocyanate was prepared from the following ingredients:

5

Polyol Package

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
	Polycarbonate Polyol ¹ (70% solution in methyl amyl ketone)	26.06
10	Methyl isobutyl ketone	21.33
	TINUVIN 328	0.50
	TINUVIN 292	0.50
	SLIP-AYD SL18	0.83
	Dow Corning Additive 11	0.03

15 ¹ Polycarbonate Polyol is commercially available from PPG Industries, Inc. as DURACARB 120.

Polyisocyanate Package

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
20	Isocyanurate derived from isophorone diisocyanate ¹ (70% solids in a 2/1 blend of SOLVESSO 100 ² /n-butyl acetate)	21.33
	Dibutyltin dilaurate	0.08

25 ¹ Available from Chemische Werke Huls AC as T1890L.

² SOLVESSO 100 is a high boiling naphtha (b.p. range 322-350°F) available from Exxon Co.

The two packages were stirred together to form a coating composition which was spray applied to a 1.5 liter polyethylene terephthalate refillable carbonated beverage bottle. The coating was cured in an electric oven at 60°C. for 15 minutes. The coated bottles were evaluated for stress cracking as described in Example 1. The results are reported in the Table below.

35

Example 5

A mixture-curable polyurethane coating composition was prepared from the following mixture of ingredients:

WO 92/19505

PCT/US92/01371

- 14 -

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
	Moisture-curable polyurethane ¹	487.5
	TINUVIN 328	2.9
	TINUVIN 292	2.9
5	Wax of Example 1	0.58
	Dibutyltin dilaurate	0.1
	Xylene	155.0

¹ Moisture-curable polyurethane available from Spencer Kellogg as SPENLITE M22-X-40.

10 The coating composition was spray applied to a 1.5 liter polyethylene terephthalate refillable carbonated beverage bottle. The coating was permitted to cure at 60°C. for 15 minutes. The coated bottles were then evaluated for stress cracking as described in Example 1. The results are reported in the Table below.

15

Comparative Example 6

For the purposes of comparison a two-package thermosetting polyepoxide-polyamine coating composition was prepared and used to coat polyethylene terephthalate bottles as generally described in 20 Examples 1-5. The coating composition was prepared from the following ingredients:

	<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
	EPON 828 ¹	27.44
25	DOWANOL PM ²	33.76
	SF-1023	0.02
	TINUVIN 328	0.52
	TINUVIN 292	0.52
	SLIP-AYD SL18	0.86
30	Dow Corning Additive 11	0.04

¹ EPON 828 is a diglycidyl ether of bisphenol A available from Shell Chemical Company.

²DOWANOL PM is propylene glycol monomethyl ether available from Dow Chemical Co.

35

WO 92/19505

PCT/US92/01371

- 15 -

Amine Package

<u>Ingredients</u>	<u>Parts by Weight (in grams)</u>
ANCAMINE 1916 ¹	6.86

¹ ANCAMINE 1916 is an epoxy-amine adduct available from
5 Pacific Anchor Chemical Co.

The two packages were stirred together to form a coating composition which was spray applied to a 1.5 liter polyethylene terephthalate refillable carbonated beverage bottle that was corona treated before coating with a Model BD-20 Treater from
10 Electro-Technics Products, Chicago, Illinois. The coating was cured in an electric oven at 60°C. for 20 minutes. The coated bottles were evaluated for stress cracking as described in Example 1. The results are reported in the Table below.

15 Testing for Stress Cracking

After the coating composition has been applied to the polyethylene terephthalate bottles and cured, the coated bottle is aged for about 16 hours at ambient conditions and the bottles tested by exposing them to the following cycle.

20 Caustic Wash: The bottles are soaked in a 3-4 percent by weight sodium hydroxide solution which contains about 0.2 percent by weight of a surfactant (Henkel P3 STABILON AL FLUESSIG) at a temperature of 138-140°F. (59-60°C.) for 15 minutes.

Pressurizing: After the bottles are removed from the
25 caustic immersion, they are given a rinse with tap water and three-quarters filled with tap water. Air pressure is applied to simulate carbon dioxide pressures with a gauge reading of 60 psi and held for 3 minutes.

Abrasion Testing on Conveyor: After the pressure is
30 released but while the bottles are still three-quarters filled with tap water, the bottles are put on a stainless steel track conveyor which is lubricated (with 0.25 percent by weight solution of Henkel P3 KET-W5). The bottles remain stationary on the conveyor while the lubricated steel conveyor moves under them for four minutes at up to
35 60 feet per minute. This part of the cycle abrades the coating in

WO 92/19505

PCT/US92/01371

- 16 -

the base area of the bottle as might happen on a filling line in a bottling plant.

The coated bottles are subjected to up to 30 cycles (caustic washing-pressurizing-abrasion testing = 1 cycle) of testing and then 5 examined for stress cracking. The results are reported in Table I below.

Table I

	<u>Coated Bottle of Example</u>	<u>Results</u>
10	1	Passes 20 cycles with good retention of clarity and adhesion, very few stress cracks in base area
15	2	Same as Example 1
	3	Passes 15 cycles with good retention of clarity and adhesion, few stress cracks in base area
20	4	Same as Example 1
	5	Same as Example 1
25	Comparative Example 6	Passes 10 cycles with good retention of clarity but beyond that point large stress cracks appear. Also, more loss of adhesion than in Examples 1-5
30	Control (polyethylene terephthalate bottle with no coating)	Passes only 3-5 cycles before extensive stress cracking is observed

35

Note, all bottles with coatings show various degrees of wear through of coatings from the conveyor testing. The ranking of the coatings for abrasion resistance is 1 = 2 = 4 > 3 = 5 > 6.

40

Example 7

The following example shows the effect of coating only the base area of a non-returnable, stand alone, polyethylene terephthalate bottle with protruding feet (Johnson Controls BIG FOOT bottles), with the polyurethane coatings of Examples 1 and 2. The 45 bottles were coated on their bottom areas only and the coating baked

WO 92/19505

PCT/US92/01371

- 17 -

at 140°F. (60°C.) for 15 minutes. Coated bottles were filled to ninety (90) percent of their volume with tap water and air pressurized to 60 psig. The pressurized bottles were then soaked at 75-80°F. (24-27°C.) in deionized water and in a lubricating solution 5 for various times as shown in Table II below and the effects of the soaking on stress cracking reported. As a control, an uncoated bottle was also tested. The results are reported in Table II below.

Table II

10 Test Time in Hours	<u>Soaking Liquid</u>		<u>Coating of Example 1</u>	<u>Coating of Example 2</u>	Control (no coating)
	<u>Deionized Water</u>	<u>Lubricating Solution¹</u>			
1	X				no effect
15	2	X			slight crazing
	4	X			slight crazing
20	20	X			medium crazing
25	1	X			medium crazing
	20	X			heavy crazing
30	20	X	no effect		"
	40 ²	X	no effect		"
35	20	X		no effect	"
	40 ²	X		very slight crazing	"

¹ 1.25 Percent by weight solution of Henkel P3 KET-W5.

40 ² End of test.

WO 92/19505

PCT/US92/01371

- 18 -

CLAIMS:

1. A pressurizable thermoplastic container having a polyurethane layer on the exterior surface thereof.
5
2. The article of Claim 1 in which the thermoplastic is a saturated polyester.
3. The article of Claim 1 in which the saturated polyester
10 is polyethylene terephthalate.
4. The article of Claim 1 which is prepared by a blow molding technique.
- 15 5. The article of Claim 4 in which the pressurizable container is a refillable bottle for carbonated beverages.
6. The article of Claim 1 in which the polyurethane layer is derived from an organic polyisocyanate and polymeric polyol.
20
7. The article of Claim 6 in which the polyurethane layer is derived from an organic polyisocyanate, a polymeric polyol and a catalyst for urethane formation.
- 25 8. The article of Claim 6 in which the polymeric polyol is selected from the class consisting of polyester polyols, polyether polyols, polycarbonate polyols, acrylic polyols and mixtures thereof.
9. The article of Claim 6 in which the polyisocyanate is
30 an aliphatic polyisocyanate.
10. The article of Claim 1 in which the polyurethane layer has a dry film thickness of 0.2 to 1.5 mils.
- 35 11. The article of Claim 1 in which the thermoplastic container has a wall thickness of 22 to 26 mils.

WO 92/19505

PCT/US92/01371

- 19 -

12. The article of Claim 1 in which the polyurethane layer contains ingredients selected from the class consisting of ultraviolet light absorbers, anti-oxidants, slip agents, anti-mar agents and mixtures thereof.

5

13. A process for protecting a pressurizable thermoplastic container prepared by the blow molding process from stress cracking by applying a continuous film of a polyurethane over the exterior surface of the thermoplastic container.

10

14. The process of Claim 13 in which the thermoplastic is a saturated polyester.

15. The process of Claim 14 in which the saturated polyester is polyethylene terephthalate.

16. The process of Claim 13 in which the pressurizable container is a refillable bottle for carbonated beverages.

17. The process of Claim 13 in which a continuous film of the polyurethane is applied by a coating process over the exterior surface of the thermoplastic container.

18. The process of Claim 17 in which the polyurethane is spray applied.

19. The process of Claim 13 in which the polyurethane is derived from an organic polyisocyanate and a polymeric polyol.

20. The process of Claim 19 in which the polyurethane is derived from an organic polyisocyanate, a polymeric polyol and a catalyst for urethane formation.

21. The process of Claim 19 in which the polymeric polyol is selected from the class consisting of polyester polyols, polyether polyols, polycarbonate polyols, acrylic polyols and mixtures thereof.

WO 92/19505

PCT/US92/01371

- 20 -

22. The process of Claim 19 in which the polyisocyanate is an aliphatic polyisocyanate.

23. The process of Claim 13 in which the polyurethane is applied as a continuous film having a dry film thickness of 0.2 to 1.5 mils.

24. The process of Claim 13 in which the film of polyurethane contains ingredients selected from the class consisting of ultraviolet light absorbers, anti-oxidants, slip agents, anti-mar agents and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01371

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5): B65D 25/34, B28B 19/00; B05D 1/36		
U.S. CL. 428/35.7, 423.7; 264/129; 427/412.5		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System ¹	Classification Symbols	
U.S.	428/35.7, 36.8, 423.1, 424.2; 264/129; 427/412.5	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁴ with indication, where appropriate, of the relevant passages ¹⁵	Relevant to Claim No. ¹⁴
<u>X</u>	US, A, 4,569,869 (KUSHIDA) 11 FEBRUARY 1986	1-3, 5, 12
Y	See the entire document.	4, 6-11, 13-24
Y	US, A, 4,785,948 (STRASSHEIMER) 22 NOVEMBER 1988 See column 1, lines 14-21.	4, 13-24
Y	US, A, 4,496,517 (KINOSHITA) 29 JANUARY 1985 See column 1, lines 9-56.	4, 13-24
Y	US, A, 4,731,289 (COLEMAN) 15 MARCH 1988 See column 2, line 12 through column 3, line 6.	6-11, 13-24
A	US, A, 4,751,120 (YAZAKI) 14 JUNE 1988 See entire document.	1-24
<p>⁶ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ³	
30 JUNE 1992	10 JUL 1992	
International Searching Authority ¹	Signature of Authorized Officer ¹⁰	
ISA/US	for <i>Rena Dye</i> Rena Dye	

